

# Trace elements and individual particle analysis of atmospheric aerosols from the Antarctic peninsula

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## ABSTRACT

Atmospheric aerosols were sampled continuously since December 1985 at the Brazilian Antarctic Station "Comandante Ferraz", (62°05'S; 58°23.5'W) on the King George Island, Antarctic Peninsula. Stacked Filter Units (SFU) were used to collect fine ( $d_p < 2.0 \mu\text{m}$ ) and coarse ( $2.0 \mu\text{m} < d_p < 15 \mu\text{m}$ ) particles on Nuclepore filters. The concentration of elements with  $Z > 10$  was measured by particle-induced X-ray emission (PIXE) analysis. This yielded data for the concentration of 23 elements: Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Se, Br, Rb, Sr, Zr and Pb. The fine and coarse aerosol mass concentration was determined by gravimetric analysis. Absolute principal factor analysis (APFA) was used to obtain the aerosol elemental source profiles. Non-sea-salt sulfate showed a clear seasonal pattern, with minimum during wintertime. For summer and wintertime coarse particles, only two factors were significant, with the first having high loadings for Na, Mg, Cl, S, Sr, K, Ca, and the coarse particle mass concentration (representing sea-salt aerosol). The second factor had high loadings for Al, Si, Fe, Ti, and Ca (soil dust aerosol). For the fine mode particles three factors were differentiated, and they represented sea-salt aerosol, soil dust and sulfates. The sea-salt source profile agreed with the average sea-water elemental composition to within 20% for the elements Na, Mg, S, Cl, K, Ca and Br. The source apportionment for the coarse particle mass concentration (CPM) revealed that 86 to 89% of the CPM is accounted for by the sea-salt aerosol component, and 3.2 to 6.8% by soil dust and that 7.6 to 8.1% of the CPM could not be apportioned. For the fine particle mass concentration (FPM), sea-salt aerosol accounted for 60%, sulfates for 24 to 31%, soil dust for only 0.5 to 1.3%. The concentration of some trace elements like Cr, Ni, Cu, Zn, and Pb appeared too high, maybe due to long range transport of polluted air masses, or regional air pollution sources in the Antarctic peninsula. These data were not used in the calculations. Individual particle analysis by Electron Probe X-Ray Microanalysis (EPMA) showed a variety of particle types. The 17708 particles from 35 fine mode samples could be clustered in 9 groups: NaCl, CaSO<sub>4</sub>, CaSO<sub>4</sub> + NaCl, CaSO<sub>4</sub> + MgCl<sub>2</sub>, S, Si + NaCl, soil dust, MgCl<sub>2</sub>, pure Si. A significant number of NaCl and MgCl<sub>2</sub> particles showed small amounts of sulfur, possibly indicating reactions of these particles with gaseous sulfur compounds. Internal mixtures of silicates and marine aerosol particles were observed. Most of the sulfur in particles larger than  $0.1 \mu\text{m}$  was in the form of CaSO<sub>4</sub>, and the abundance of these particles showed a seasonal variability with maximum in summer.

## 1. Introduction

Antarctica is supposed to suffer minimally from anthropogenic pollution, although the concentrations of several trace gases are known to be increasing over this continent. The recent interest in characteristics of the Antarctic atmosphere has

resulted in a recognition of the need for long term background aerosol studies. As the Antarctic continent is far from important anthropogenic sources, it is an ideal site to follow the trends in regional (and global) concentrations of trace elements in the atmosphere. Also the ocean surrounding the Antarctic continent is very produc-

tive from the biological point of view. Several trace elements like Fe act as micronutrients (Duce, 1986; Martin and Gordon, 1988). Several recent studies have shown that the atmospheric transport and deposition of trace elements affects the chemistry and also the biology of the oceans.

Due to the surrounding ocean and very low soil dust aerosol load, the Antarctic peninsula is also an ideal site to study properties of marine aerosol particles (Mészáros and Vissy, 1974; Fitzgerald, 1991). The mechanisms of the production of marine aerosol particles are far from fully understood (Marks, 1990). The intense exchange of gases and particles at the air-sea interface is important for the global budget of several gases and particles (Sievering et al., 1982; Andreae and Raemdonck, 1983). Heterogeneous sulfur conversion in sea-salt particles occurs and is necessary to explain part of the excess sulfate observed over remote ocean areas (Sievering et al., 1991). The large diversity of particles indicates that many other mechanisms in addition to the bursting of air bubbles are taking place (Blanchard and Woodcock, 1957, 1980; Lovett, 1978; Stramska et al., 1990). In-cloud processes could be responsible for the production mechanisms of  $\text{CaSO}_4$  particles found in the marine atmosphere of remote regions (Andreae et al., 1986). During the evaporation of sea-water droplets in the atmosphere several mineral crystals are sequentially produced and released in the atmosphere (Harvie et al., 1980). Several heavy metals (e.g., Ni, Cu, Zn, Se, Sb, Pb, Cd, Ag, V, etc.) were found enriched in several studies (Maenhaut et al., 1983; Weisel et al., 1984; Arimoto et al., 1985, 1987, 1990; Zhou et al., 1990). In addition to long-range transport, biogenic agents may be responsible for some of the large enrichments of heavy metals over oceanic areas (Cattell and Scott, 1978). Fractionation in the seawater-atmosphere interface during bubble bursting processes was observed for heavy metals (Van Grieken et al., 1974), and is even important for major ions (Keene et al., 1986). Of particular interest is the sulfur cycle over marine regions (Toon et al., 1987) and the interpretation of the observed sulfate excess. Many studies have focused on the sulfur cycle over remote marine regions (Mészáros, 1978; Kritz, 1982; Andreae et al., 1985; Prospero et al., 1985, 1991; Clarke et al., 1987; Bates et al., 1989; Berresheim et al., 1989, 1990; Pszenny et al., 1989; Savoie and Prospero, 1989). The sulfur containing

particles are important because they could play a role in global climate change, influencing the radiation budget and the concentration of cloud condensation nuclei (Schwartz, 1988; Savoie et al., 1989; Götz, 1991).

Several studies of aerosol particles in the Antarctic or sub-Antarctic atmosphere have been carried out (Zoller et al., 1974; Maenhaut et al., 1979; Parungo et al., 1979, 1981; Shaw, 1980; Cunningham and Zoller, 1981; Koide et al., 1981; Dick and Peel, 1985; Ito, 1985; Bodhaine et al., 1986; Wagenbach et al., 1988; Berresheim et al., 1989; Pszenny et al., 1989; Tuncel et al., 1989; Artaxo et al., 1990b, 1990d; Harvey et al., 1991). Many of these studies were done at the geographic South Pole, which is representative for central Antarctica, but these data are difficult to compare with coastal sites. Very few of the sampling programs in Antarctica have collected aerosol particles with size-segregated samplers. The knowledge of the minor components of Antarctic aerosol is very incomplete. The combination of a multielement bulk analytical technique as PIXE coupled with individual particle analysis was never used in Antarctic aerosol studies. Only a few of the studies done so far have taken advantage of powerful multivariate techniques for aerosol source recognition and apportionment. Data from various sites at the edge of the Antarctic continent are required in order to improve our understanding of the overall continental Antarctic aerosol chemistry.

In this paper, we report on measurements of fine and coarse aerosol particles carried out in the Antarctic Peninsula. Five years of continuous aerosol sampling were performed in separate coarse and fine size fractions, with clear seasonal variability for several elements. The bulk elemental composition was measured by particle-induced X-ray emission (PIXE), and the multielement data sets obtained were examined by absolute principal factor analysis. Individual particles were analyzed by electron probe X-ray microanalysis (EPMA). More than 17,000 individual fine mode particles (with  $0.1 \mu\text{m} < d_p < 2.0 \mu\text{m}$ ) were measured and sized, giving insights on aerosol particle types and association between elements at the individual particle level. Particular emphasis was placed on studying the relation between sulfur at bulk concentrations and sulfur in the individual aerosol particles in the fine mode Antarctic aerosol.

## 2. Experimental methods

### 2.1. Sampling site and sampling procedures

The sampling station is located at the Brazilian Antarctic Station, "Comandante Ferraz" ( $62^{\circ}05'S$ ;  $58^{\circ}23.5'W$ ), in the King George Island, on the Admiral Bay, Antarctic Peninsula. Fig. 1 shows a map with the sampling station location. The sampling site is upwind from local sources, at about 1 km from the main station, and it is at about 300 m from the sea coast. The station is operated continuously since December 1985, including during the winter season.

Aerosol particles were collected with Stacked Filter Units (SFU) (Parker et al., 1977). Coarse particles ( $2.0 \mu\text{m} < d_p < 15 \mu\text{m}$ ) were sampled on a 47-mm-diameter,  $8 \mu\text{m}$  pore-size Nuclepore filter, while a  $0.4 \mu\text{m}$  pore-size Nuclepore filter collected the fine particles ( $d_p < 2.0 \mu\text{m}$ ). The flow rate was 10 to 16 l/min which resulted in a 50% cut-off diameter between fine and coarse aerosol fractions of about  $2.0 \mu\text{m}$  (John et al., 1983). The SFU were fitted with a specially designed inlet which provided a 50% cutoff diameter of  $15 \mu\text{m}$  (Cahill et al., 1979) so that only inhalable particles were sampled. Air volumes were measured with calibrated gas meters with a precision of about 5%. The SFU were loaded with the Nuclepore filters in our São Paulo clean room laboratory, transported in a sealed container, and hand-carried after the sampling. Blank filters received the same handling as exposed filters before and after sampling. The collection time per SFU sample varied between 5 and 8 days.

### 2.2. Gravimetric analysis

The fine and coarse fraction aerosol mass concentrations were obtained through gravimetric analysis of the Nuclepore filters. The filters were weighed before and after sampling in a Mettler M3 electronic microbalance with  $1 \mu\text{g}$  sensitivity. Before weighing, the filters were equilibrated for 24 h at 50% relative humidity and  $20^{\circ}\text{C}$ . Electrostatic charges were controlled by means of  $^{210}\text{Po}$  radioactive sources. The detection limit for the aerosol mass concentration is typically  $0.3 \mu\text{g m}^{-3}$  and the precision is estimated at about 15%. The coarse mode aerosol mass concentration is named CPM (coarse particle mass concentration), and the fine mode aerosol mass concentration is named FPM (fine particle mass concentration).

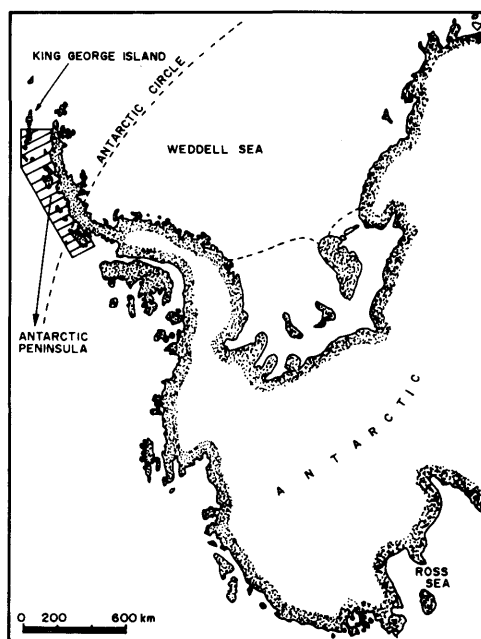
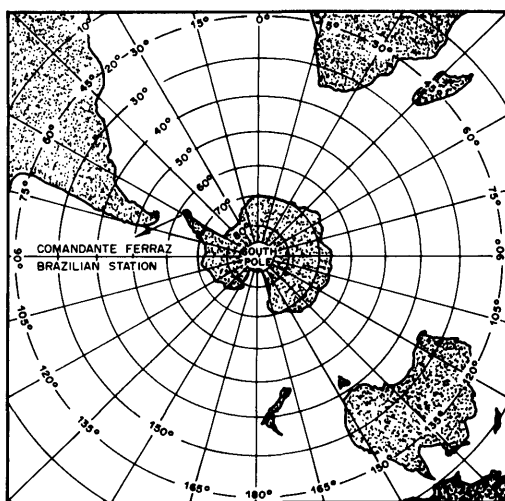


Fig. 1. Map with the sampling station location. The sampling station is located at the Brazilian Antarctic Station, "Comandante Ferraz" ( $62^{\circ}05'S$ ;  $58^{\circ}23.5'W$ ), in the King George Island, on the Admiral Bay, Antarctic Peninsula. The sampling site is upwind from local sources, at about 1 km from the main station, and it is at 300 m from the sea coast.

### 2.3. Elemental concentration measurement

The elemental concentrations were measured by particle-induced X-ray emission (PIXE) (Johansson and Campbell, 1988). The samples were irradiated by a 2.4 MeV proton beam, supplied by the isochronous cyclotron of the University of Ghent. Full details about the experimental PIXE setup, analytical procedures, calibration, and uncertainties are given elsewhere (Maenhaut et al., 1981, 1987; Maenhaut and Raemdonck, 1984). The following 23 elements were measured in the samples: Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Se, Br, Rb, Sr, Zr, and Pb. The detection limit was typically  $5 \text{ ng m}^{-3}$  for elements with  $Z < 20$ , and  $0.1 \text{ ng m}^{-3}$  for  $21 < Z < 30$ . The precision of the PIXE analysis was better than 3% for the major elements and about 10% for elements with concentrations near the detection limit.

### 2.4. Individual particle analysis by EPMA

Electron probe X-ray microanalysis (EPMA) was used for individual particle analysis (Casuccio et al., 1983; Markowicz et al., 1986; Bruynseels et al., 1988; Dzubay and Mamane, 1989; Saucy et al., 1991). A JEOLJXA-733 Superprobe equipped with backscatter and secondary electron detectors and an energy dispersive X-ray detection system were used. A Si (Li) X-ray detector coupled to a Tracor Northern TN-2000 system was employed for acquiring the X-ray spectra for elements with  $Z > 11$ , and a PDP 11/23 microcomputer controlled all EPMA parameters. Fully automated analysis can be performed and hundreds of particles can be analyzed automatically in a few hours (Storms et al., 1987; Van Borm and Adams, 1988). The automated particle recognition and characterization (PRC) software controls the beam scanning over a preset area of interest. When the backscattered electron intensity of the particle contour exceeds a threshold value, the system detects an aerosol particle. The average diameter is measured based on the projected physical particle diameter and might differ from the aerodynamic diameter. An X-ray spectrum is accumulated while the electron beam performs a star scan over the particle during 60 to 100 s. An electron energy of 20 keV and a low beam current of 1 nA were

used to avoid damage to the particles due to the electron beam. Morphological data such as the average diameter and a shape factor were obtained for each particle. The relative percentage of X-ray intensities expresses the ratio of the net X-ray intensity of that element to the total net X-ray intensities collected from that particle. The loadings of the filters were low enough for the individual particles to be well separated from each other. For each aerosol sample 300 to 1000 individual particles were automatically analyzed. The elemental detection limits of the EPMA analysis are around 1% in mass. A high magnification ( $2600\times$ ) was used, so the minimum particle size analyzed was  $0.1 \mu\text{m}$ . The reproducibility for particle sizing using the backscattered electron image is within 6% of the mean diameter.

The huge data set collected for each sample was reduced using hierarchical and non-hierarchical cluster analysis in order to classify the particles according to their elemental composition (Storms et al., 1984; Van Borm and Adams, 1988). The method starts from  $n$  particles ( $n$  from 300 to 1000) that are to be classified, and at each step the two more similar particles are merged into a single cluster. The new data set of  $n-1$  objects is again analyzed until the whole data set is reduced to few particle groups. The similarity between two pairs of particles was derived from the Euclidian distance coefficient. The Ward's error sum method was used for the calculation of the distances between newly formed groups and the remaining particles or clusters (Massart and Kaufman, 1983). The clustering was performed with the normalized X-ray intensities. For each individual filter from 6 to 10 different groups of particles could be distinguished, and the average elemental composition and diameter of each particle group were calculated.

After the analysis of the population and composition of the groups of particles for each sample, a global non-hierarchical cluster analysis was performed, involving all the samples clustered in a consistent group of particles. Each individual sample was classified in 9 fixed particle groups whose composition was derived from the analysis of the individual samples. This methodology allows easy comparisons of particle population and composition between samples. In this study 17708 individual particles were sized and analyzed in 35 different fine mode aerosol samples.

### 3. Absolute principal factor analysis

The elemental composition of particulate matter sources can be studied with the use of receptor models (e.g., Chemical Mass Balance, Stepwise Multiple Regression, Factor Analysis, Cluster Analysis, etc.) (Hopke, 1985; Artaxo and Orsini, 1987; Gordon, 1988). In the present study we were interested in identifying the sources of aerosols in the Antarctic peninsula and extracting their elemental compositions through the use of absolute principal factor analysis (APFA) (Thurston and Spengler, 1985). APFA offers the possibility to obtain a quantitative source profile instead of only a qualitative factor loading matrix as in traditional applications of factor analysis. The elemental source profiles help in the identification of the factors and can be used to compare the factor compositions with the assumed aerosol sources.

In principal factor analysis (Harman, 1976) a model of the variability of the trace element concentrations is constructed so that the set of inter-correlated variables is transformed into a set of independent, uncorrelated variables. This is done by finding the eigenvalues and eigenvectors of the correlation matrix. The most prominent eigenvectors (factors) are retained and orthogonally rotated by a VARIMAX rotation. The resulting "factor-loading" matrix represents the correlations between the trace elements and each orthogonal factor. Also "factor scores" are calculated which indicate the relative importance of each factor for the individual samples (Heidam, 1982). In a normal application, factors that have eigenvalues larger than approximately 1.0 after VARIMAX rotation are retained (Hopke, 1985).

The APFA procedure obtains the elemental mass contribution of each identified component by calculating the absolute principal factor scores (APFS) for each sample (Thurston and Spengler, 1985). The elemental concentrations are subsequently regressed on the APFS to obtain the contribution of each element for each component. The source profiles thus obtained can be compared with values from the literature to gain information on enrichment and atmospheric chemistry processes. The measured aerosol mass concentration can also be regressed on the APFS in order to obtain the aerosol total mass source apportionment (Heidam, 1982).

### 4. Results and discussion

The PIXE analysis was performed on samples collected from 1985 to 1988, making a total of 115 fine and coarse mode Antarctic aerosol samples. The average elemental concentrations for the fine mode samples are presented in Table 1. In the first column average values for all samples are presented, while in the second and third columns averages for samples collected during summertime and wintertime are given. Even for the fine mode aerosol fraction the strong dominance of sea-salt elements is evident. The concentrations of elements associated with soil dust were very low. The sulfur concentration in the fine mode was  $97.4 \text{ ng m}^{-3}$ . The average non-sea-salt sulfur concentration is  $72.5 \text{ ng m}^{-3}$ , obtained by subtracting sea-salt sul-

Table 1. Average elemental concentrations for fine mode antarctic aerosol; particles with  $d_p < 2.0 \mu\text{m}$

Element	Concentration ( $\text{ng m}^{-3}$ )					
	All samples		Summer-time*		Winter-time*	
Na	288.4	(115)	291.8	(57)	285.1	(58)
Mg	34.3	(115)	33.9	(57)	34.7	(58)
Al	2.99	(55)	2.39	(21)	3.37	(34)
S	97.4	(115)	125.2	(57)	70.1	(58)
Cl	533.2	(115)	493.1	(57)	572.6	(58)
K	15.1	(115)	14.9	(57)	15.3	(58)
Ca	16.7	(115)	17.1	(57)	16.3	(58)
Ti	0.16	(10)	0.15	(8)	0.19	(2)
Cr	1.24	(20)	1.89	(6)	0.97	(14)
Mn	0.17	(9)	0.23	(5)	0.095	(4)
Fe	0.75	(93)	1.01	(52)	0.42	(41)
Ni	0.082	(7)	0.076	(6)	0.12	(1)
Cu	0.17	(53)	0.18	(27)	0.16	(26)
Zn	1.79	(109)	1.45	(54)	2.11	(55)
Pb	0.18	(28)	0.20	(12)	0.16	(16)
Se	0.061	(36)	0.064	(30)	0.045	(6)
Br	2.99	(103)	2.19	(57)	3.99	(46)
Rb	0.22	(10)	0.13	(4)	0.28	(6)
Sr	0.32	(101)	0.31	(46)	0.32	(55)
NSS_S (*)	72.5	(115)	102.2	(57)	43.3	(58)
FPM (*)	2.37	(115)	2.21	(57)	2.52	(58)

\* Summer-time: samples collected from 1 November to 30 April. Winter-time: samples collected from 1 May to 31 October. The number of samples with concentration above the detection limit is in parentheses. NSS\_S is non-sea-salt sulfur obtained after subtracting sea-salt sulfur. FPM is the fine particle mass concentration ( $\mu\text{g m}^{-3}$ ).

fur with data from Riley and Chester (1971), and using chlorine as sea-salt reference element. The aerosol mass concentration was  $2.37 \mu\text{g m}^{-3}$  in the fine mode. The concentrations of trace elements that could be associated with anthropogenic sources, like Cr, Ni, Cu and Pb are very small, but are somewhat higher than values reported for other stations in Antarctica (Zoller et al., 1974; Wagenbach et al., 1988; Tuncel et al., 1989). It is difficult to compare aerosol concentrations measured with different samplers and during different periods where seasonal variations are large, but for sulfur our results are about 30% higher than those measured at the German Antarctic station (located in the Antarctic coastal region at  $70^\circ\text{S}$ ,  $8^\circ\text{W}$ ) with a high volume sampler operated continuously from 1983 to 1985 (Wagenbach et al., 1988). Lawson and Winchester (1978, 1979) report fine mode sulfur concentrations in the range of 52 to  $98 \text{ ng m}^{-3}$  for the Southern tip of South America. They also report  $60 \text{ ng m}^{-3}$  fine mode and  $87 \text{ ng m}^{-3}$  coarse mode sulfur measured in Samoa ( $14^\circ\text{S}$ ,  $170.5^\circ\text{W}$ ), values very similar to the ones observed in this work. Savoie and Prospero (1989) measured non-sea-salt sulfate values of 220 to  $400 \text{ ng m}^{-3}$  for several remote sites in the South Pacific. Our results are near this range, with a non-sea-salt sulfate yearly average of  $217 \text{ ng m}^{-3}$  and a summertime average of  $307 \text{ ng m}^{-3}$ . There is a strong seasonality of average concentrations for several elements, with higher values during summertime. For several elements like Ni, Cu, Zn, Cr, Pb the values in Table 1 should be considered as upper limit concentrations. Certainly local and regional sources give some contribution to the concentration of some of these elements. From time to time in the region, there are ships, helicopters and other vehicles that have high emissions to the atmosphere. Also diesel generators from several research stations on the Antarctic peninsula can be responsible for part of the presence of these elements (Boutron and Wolff, 1989). Our Pb concentration is similar to other measurements taken at the Antarctic peninsula during summer 1979–1980 (Peel and Wolf, 1982).

Table 2 presents the average elemental concentrations for the coarse mode aerosol fraction. Sea-salt aerosol dominates, and soil dust related elements are present in very low amounts. Even in the coarse mode, non-sea-salt sulfur at  $38.3 \text{ ng m}^{-3}$  represents 43% of the total coarse

mode sulfur concentration. Non-sea-salt sulfur is higher during summertime, as expected for marine biogenic sulfur sources.

In order to study the characteristics of the average elemental concentrations, enrichment factors (EF) were calculated using Cl as tracer for sea-salt aerosol and the following expression:

$$\text{EF(X)} = \frac{[\text{C(X)/C(Cl)}]_{\text{aerosol}}}{[\text{C(X)/C(Cl)}]_{\text{sea-water}}},$$

where C(X) is the concentration of the element X for the aerosol or the reference sea-water. As reference composition for bulk sea-water, data from Riley and Chester (1971) were used. Fig. 2 presents the EF values calculated for the fine and

Table 2. Average elemental concentration for coarse mode antarctic aerosol; particles with  $2.0 \mu\text{m} < d_p < 15.0 \mu\text{m}$

Element	Concentration ( $\text{ng m}^{-3}$ )			
	All samples	Summer-time*	Winter-time*	
Na	668.8 (115)	754.4 (57)	584.8	(58)
Mg	76.9 (115)	85.5 (57)	68.6	(58)
Al	8.81 (81)	10.9 (46)	6.10	(35)
Si	19.9 (76)	24.0 (45)	14.1	(31)
S	89.7 (115)	104.2 (57)	75.5	(58)
Cl	1101.0 (115)	1206.7 (57)	996.9	(58)
K	31.9 (115)	34.3 (57)	29.7	(58)
Ca	35.1 (115)	40.8 (57)	29.5	(58)
Ti	1.15 (65)	1.43 (39)	0.74	(26)
Cr	0.57 (23)	0.38 (9)	0.69	(14)
Mn	0.34 (45)	0.43 (29)	0.16	(16)
Fe	8.11 (115)	12.1 (57)	4.21	(58)
Ni	0.15 (23)	0.16 (10)	0.15	(13)
Cu	0.82 (85)	0.61 (44)	1.04	(41)
Zn	5.50 (115)	5.74 (57)	5.27	(58)
Pb	0.65 (47)	0.60 (16)	0.67	(31)
Se	0.068 (3)	0.058 (1)	0.073	(2)
Br	4.65 (115)	4.21 (57)	5.09	(58)
Rb	0.23 (1)	0.23 (1)	—	(0)
Sr	0.63 (115)	0.73 (57)	0.53	(58)
NSS_S (*)	38.3 (115)	47.8 (57)	28.9	(58)
CPM (*)	4.40 (115)	5.03 (57)	3.77	(58)

\* Summer-time: samples collected from 1 November to 30 April. Winter-time: samples collected from 1 May to 31 October. The number of samples with concentration above the detection limit is in parentheses. NSS\_S is non-sea-salt sulfur obtained after subtracting sea-salt sulfur. CPM is the coarse particle mass concentration ( $\mu\text{g m}^{-3}$ ).

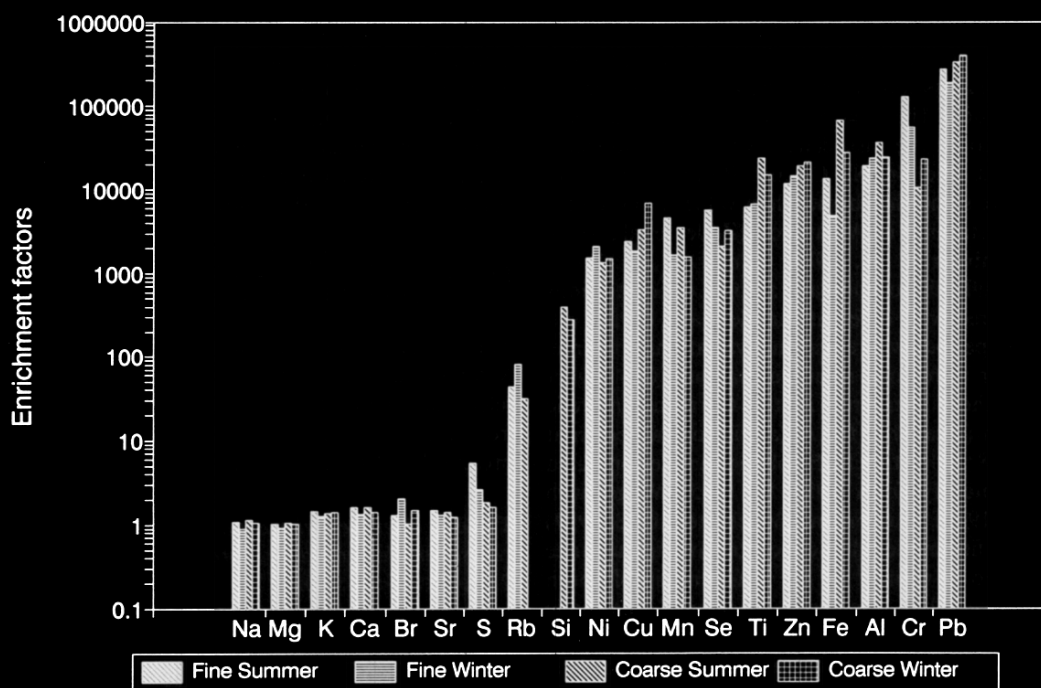


Fig. 2. Enrichments factor (EF) values calculated for the fine and coarse mode in wintertime and summertime samples. As reference composition for bulk sea-water, data from Riley and Chester (1971) were used.

coarse mode in wintertime and summertime samples. Some elements (Na, Mg, K, Ca, Br, Sr, S) have enrichment factors near 1, indicating their marine origin. A 2nd group of elements that generally have the earth crust as main source (Al, Si, Ti, Mn, Fe) are enriched by three to five orders of magnitude. A 3rd group of elements (Ni, Cu, Zn, Se, Cr, Pb) have very high enrichment factor values. Similar EFs for some of these elements were also observed by Tuncel et al. (1989) at the South Pole. Some of these heavy metals can be transported from the ocean to the atmosphere (Weisel et al., 1984). From this work it is not possible to clearly identify the source or sources of the latter group of elements. As already discussed, local and regional sources of air pollution can give some contribution to the concentration of some of these elements. Also, fractionation mechanisms are known to enrich sea-water droplets with heavy metals like Zn (Van Grieken et al., 1974), Cu (Cattell and Scott, 1978) and others.

There is no clear seasonal variability for the fine or coarse mode aerosol mass concentration.

Typically the fine mode mass concentration is a very low  $2 \mu\text{g m}^{-3}$ , whereas the coarse mode is  $4 \mu\text{g m}^{-3}$  during wintertime and  $5 \mu\text{g m}^{-3}$  during summertime. Fig. 3 shows the fine and coarse mode seasonal variability for the non-sea-salt sulfur concentration. There is a seasonality in the fine mode non-sea-salt sulfur concentration, in accordance to other studies (Prospero et al., 1991; Wagenbach et al., 1988), probably because of the biogenic origin. During wintertime the non-sea-salt sulfur concentration values are about  $10\text{--}40 \text{ ng m}^{-3}$ , reaching  $150\text{--}300 \text{ ng m}^{-3}$  during summertime. The coarse mode non-sea-salt sulfur, shown in the lower part of Fig. 3, also exhibits some seasonal variability, but not so clear as for the fine mode. Typical values of coarse mode non-sea-salt sulfur are about  $40 \text{ ng m}^{-3}$ . This coarse mode non-sea-salt sulfur can be partially explained by reactions of sulfur gases on existing coarse mode marine aerosol particles. This will be further discussed with the individual particle analysis data.

The variability of the elemental concentrations

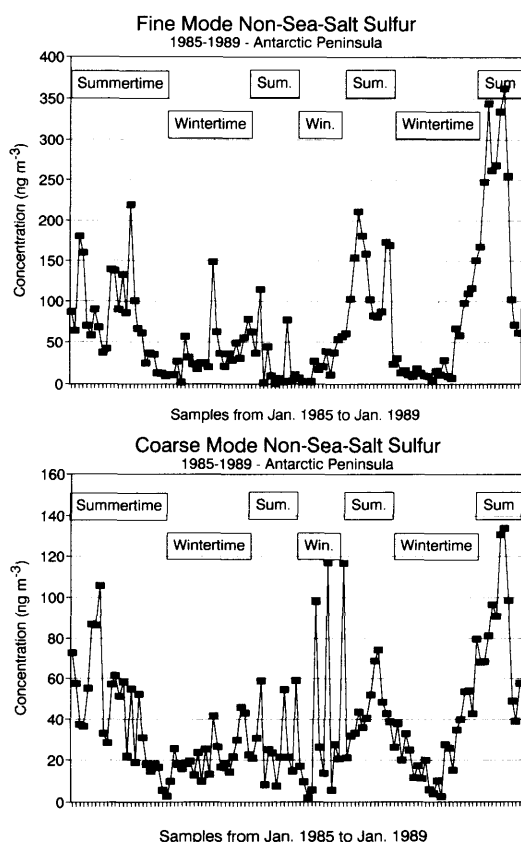


Fig. 3. Fine and coarse mode seasonal variability of the non-sea-salt sulfur concentration.

was analyzed by Absolute Principal Factor Analysis (APFA). Three analyses were done: one with all samples ( $n = 115$ ), one including only samples collected during summertime (1 November to 30 April) ( $n = 57$ ), and the last analysis included only samples collected during wintertime (1 May to 31 October) ( $n = 58$ ). Only elements that were detected in all samples were used in the factor analysis calculation in order to avoid problems with the estimation of the missing values. Elements that are possibly influenced by regional air pollution sources like Pb, Zn, Cu and others, were not included in the Factor Analysis calculations. For all APFA calculations for the coarse mode, only two factors were statistically significant, and they explained more than 87% of the data variability for the APFA with all samples, 88% for the summertime APFA, and 85% for the wintertime

Table 3. VARIMAX rotated factor loading matrix for antarctic coarse mode aerosol

Summer- and winter-time	Sea-salt	Soil
Na	0.82	0.12
Mg	0.97	-0.01
Al	0.19	0.96
Si	0.05	0.94
S	0.91	0.12
Cl	0.95	0.06
K	0.93	0.08
Ca	0.85	0.44
Ti	0.12	0.97
Fe	0.01	0.98
Br	0.75	-0.18
Sr	0.84	0.40
CPM	0.92	0.16

Summer-time	Sea-salt	Soil
Na	0.80	0.08
Mg	0.96	-0.07
Al	0.13	0.97
Si	0.05	0.95
S	0.94	0.08
Cl	0.96	0.01
K	0.96	0.13
Ca	0.80	0.49
Ti	0.11	0.97
Fe	-0.03	0.98
Br	0.84	-0.21
Sr	0.82	0.38
CPM	0.93	0.16

Winter-time	Sea-salt	Soil
Na	0.84	0.04
Mg	0.98	0.00
Al	0.27	0.94
Si	0.02	0.93
S	0.90	0.03
Cl	0.94	0.07
K	0.89	0.05
Ca	0.92	0.26
Fe	-0.02	0.95
Br	0.79	0.07
Sr	0.88	0.35
CPM	0.94	0.02

APFA. Communalities for all analyses and all elements are typically larger than 85%. Table 3 shows the factor loading matrix after VARIMAX rotation for the APFA of the coarse mode data set. For summer and winter-time the first factor is highly loaded with Na, Mg, S, Cl, K, Ca, Br, Sr, and CPM, indicating that it represents sea-salt



aerosol particles. The second factor has high correlations with Al, Si, Ti, and Fe, and clearly represents soil dust aerosol. This soil dust component can originate from the Antarctic peninsula or from the Southern tip of the South American continent, as deduced from radon measurements at our station (Pereira, 1990). Although most of the Ca and Sr are associated with sea-salt aerosol, they have moderate loadings for the soil dust factor, indicating that a small part of their variability is associated with soil dust aerosol. Sulfur is associated only with sea-salt aerosol in the coarse aerosol fraction.

For the fine mode, three factors were statistically

Table 4. VARIMAX rotated factor loading matrix for antarctic coarse mode aerosol

Summer- and winter-time	Sea-salt	sulfate	soil dust
Na	0.94	0.25	0.04
Mg	0.96	0.19	0.02
S	0.19	0.95	0.12
Cl	0.99	0.01	-0.01
K	0.97	0.16	0.09
Ca	0.96	0.10	0.10
Fe	0.04	0.09	0.97
Br	0.71	0.31	-0.22
Sr	0.90	0.20	0.10
FPM	0.81	0.48	-0.02

Summer-time	sea-salt	sulfate	soil dust
Na	0.92	0.34	0.04
Mg	0.94	0.25	0.02
S	0.15	0.97	0.04
Cl	0.99	0.01	0.00
K	0.95	0.20	0.11
Ca	0.96	0.09	0.10
Fe	0.09	0.03	0.99
Br	0.77	0.47	0.05
Sr	0.90	0.15	0.14
FPM	0.77	0.55	-0.03

Winter-time	sea-salt	sulfate	soil dust
Na	0.94	0.25	0.08
Mg	0.95	0.24	0.03
S	0.20	0.92	0.20
Cl	0.98	0.17	-0.04
K	0.95	0.24	0.11
Ca	0.96	0.22	0.01
Fe	0.07	0.09	0.97
Br	0.55	0.63	-0.22
Sr	0.87	0.36	0.08
FPM	0.77	0.49	0.26

significant for all data sets. Table 4 presents the factor loading matrix for the fine mode APFA calculations. The first factor is highly loaded with Na, Mg, Cl, Ca, Br, Sr, and FPM, clearly indicating sea-salt aerosol. The second factor has a high loading only for sulfur, and was named sulfate. The third factor has a high loading only for Fe, indicating the soil dust. Due to the very low concentration of soil dust particles, it was not possible to measure Al, Si and Ti in the fine mode in a significant number of samples. Sulfur has a small but significant loading for the sea-salt factor, indicating that for the fine mode small amounts of sulfur are associated with the sea-salt component. Calcium has a significant loading for the winter-time sulfate component. The fine mode aerosol mass concentration also has a significant loading for the sulfate component.

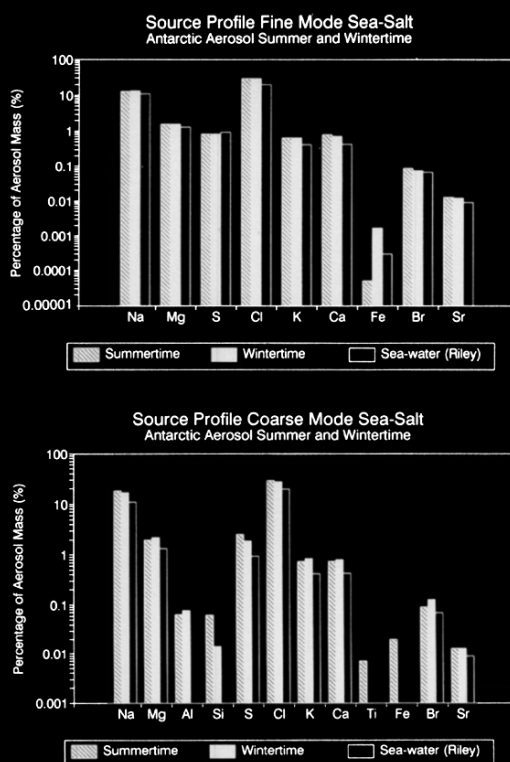


Fig. 4. Fine and coarse mode elemental profiles for the sea-salt aerosol component for summer and wintertime APFA analysis. The elemental concentrations are represented as percentage of the total aerosol mass. For comparison, also the average sea-water composition from Riley and Chester (1971) is shown.

In order to obtain the elemental profiles of these factors, the elemental concentrations were regressed with the absolute factor scores according to the procedure developed by Thurston and Spengler (1985). Fig. 4 shows the fine and coarse mode elemental profile for the sea-salt aerosol component for the summer and wintertime APFA analysis. The elemental concentrations are represented as percentage of the total aerosol mass. For comparison, also the average sea-water composition from Riley and Chester (1971) is shown. The agreement between the obtained source profiles and the average sea-water composition is remarkable. Even for elements that are present in concentrations of less than 0.1 % in mass (Br, Sr) the agreement is very good. For Al, Si, Ti and Fe the largest contribution in the atmosphere is the soil dust particles, that could have a small common variability with the marine component.

Fig. 5 shows the fine mode aerosol source apportionment for the summer and wintertime samples. Sea-salt aerosol dominates the mass in the fine fraction, with very low abundance of the soil dust component (1.3 % for summertime and 0.5 % for wintertime). The sulfate component is responsible for a significant fraction of the fine mode mass, accounting for 31 % of the fine mass

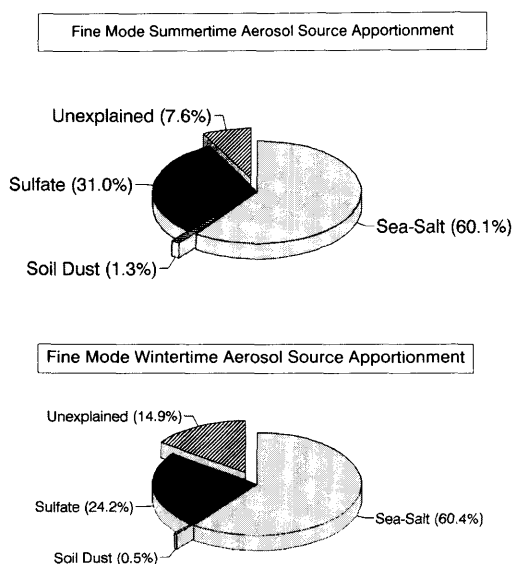


Fig. 5. Fine mode aerosol mass concentration source apportionment for summer and wintertime samples.

during summertime and 24 % during wintertime. The coarse mode aerosol mass source apportionment for the summer and wintertime data sets shows that sea-salt aerosol accounts for 86 % and 89 % of the aerosol mass in the coarse mode. As expected, coarse mode soil dust exhibits a smaller presence in wintertime (3.2 %) than during summertime (6.8 %). The unexplained mass in the fine and coarse source apportionment could be water in the samples or organic material that cannot be traced using the elemental concentrations obtained by PIXE.

A different view of the properties of the Antarctic aerosol particles can be obtained by analyzing the individual aerosol particles by EPMA. Fig. 6 shows some electron microprobe pictures of typical particles found in the coarse mode filters. NaCl,  $\text{MgCl}_2$ ,  $\text{CaSO}_4$ ,  $(\text{NH}_4)_2\text{SO}_4$ , soil dust and other types of particles are present in the Antarctic atmosphere, and some of them could easily be discriminated by their morphology.  $\text{CaSO}_4$  can be observed in two types of morphology: as round particles or as long needles, and this depends on the way the particle was formed (Andreae et al., 1986).

For the fine mode samples, for particles larger than  $0.1 \mu\text{m}$  a very large number of particles (17708) in 35 different samples collected over a period of 3 years was analyzed. Fig. 7 presents the 7 groups of particles that were discriminated by the cluster analysis procedure for the fine mode aerosol particles. NaCl particles account for 76.6 % of the number of particles. Particles containing only sulfur as detected element account for a very low 2.3 % of the number of particles. Pure  $\text{CaSO}_4$  and  $\text{CaSO}_4$  mixed with NaCl and  $\text{MgCl}_2$  account for 9.4 %. Soil dust particles account only for 1.1 %. The group of particles containing only Si shows a morphology suggesting that they are skeletons of marine organisms. There is a significant fraction of particles that are an internal or external mixture of different sea-salt aerosol particle types. Particles in internal mixture like  $\text{CaSO}_4$  together with NaCl or  $\text{MgCl}_2$  together with NaCl account for about 10 % of the particle population. This type of complex particles was already observed in other studies in Antarctica (Parungo et al., 1979; Harvey et al., 1991) and in the remote marine atmosphere (Andreae et al., 1986).

The most striking result of Fig. 7 is that in the

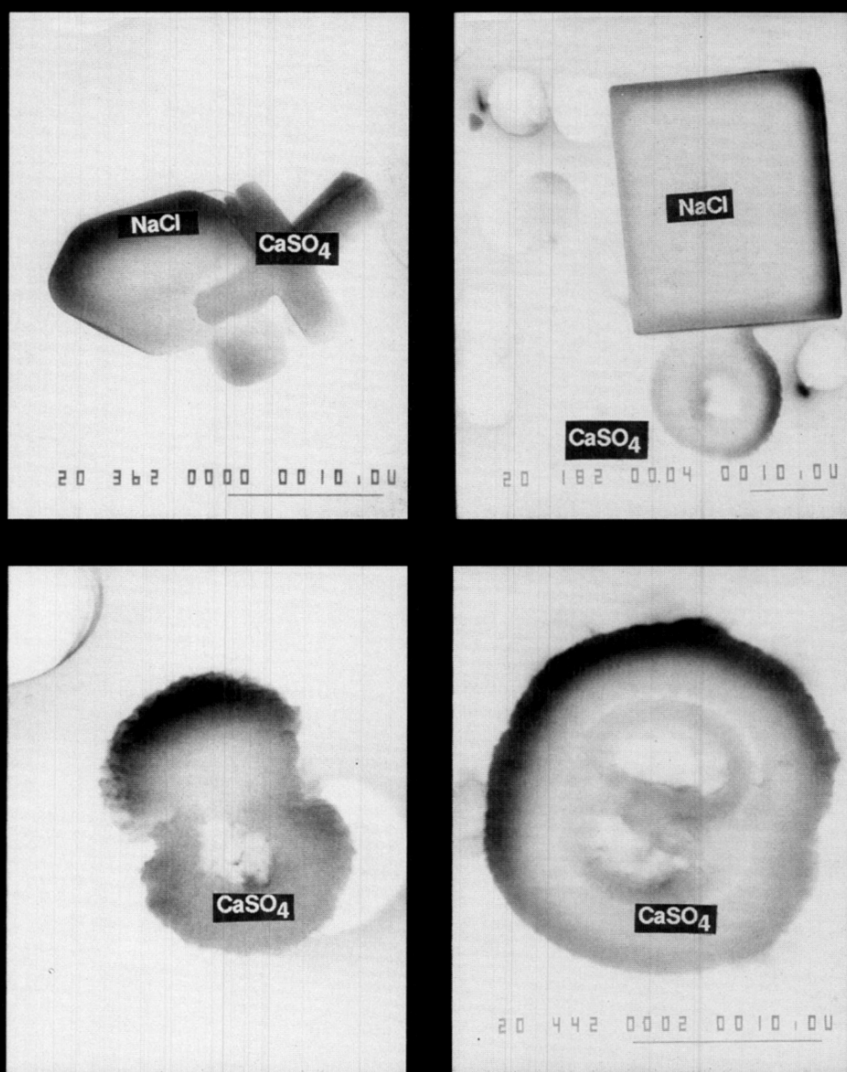


Fig. 6. Electron microscopy pictures of typical particles found in the coarse mode filters. In the upper left, a mixed NaCl and  $\text{CaSO}_4$  particle. In the upper right a similar mixture, but with different morphology for the  $\text{CaSO}_4$  particle. The two pictures at the bottom are  $\text{CaSO}_4$  particles. The bar on the lower right correspond to a size of  $10\ \mu\text{m}$ .

fine mode aerosol particles from the Antarctic peninsula, sulfur appears predominantly as  $\text{CaSO}_4$  instead of  $(\text{NH}_4)_2\text{SO}_4$  or  $\text{NH}_4\text{HSO}_4$ . It is important to indicate that only particles larger than  $0.1\ \mu\text{m}$  were analyzed. Although typically about 70% of the number of particles containing  $(\text{NH}_4)_2\text{SO}_4$  or  $\text{NH}_4\text{HSO}_4$  are in the range  $0.03\ \mu\text{m} < r < 0.1\ \mu\text{m}$  (Mészáros, 1991), it is surprising to find here such a large percentage of

$\text{CaSO}_4$  particles versus  $(\text{NH}_4)_2\text{SO}_4$  for particles larger than  $0.1\ \mu\text{m}$ . We investigated some possible analytical artifacts that could influence this result. The samples were analyzed in vacuum, so it would be possible that some of the  $(\text{NH}_4)_2\text{SO}_4$  or  $\text{NH}_4\text{HSO}_4$  particles could have been lost because of the in-vacuum analysis. Intercomparison of in-vacuum sulfur analysis versus measurements of sulfate by ion chromatography shows that

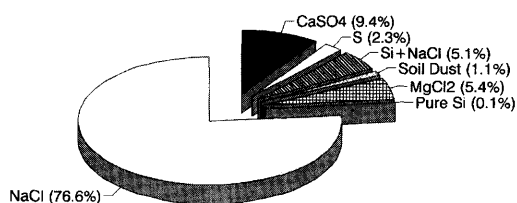


Fig. 7. Aerosol particle types in the Antarctic peninsula. Individual particle analysis of 17708 particles in 35 fine mode samples ( $0.1 \mu\text{m} < d_p < 2.0 \mu\text{m}$ ).

this is not the case. Agreements better than 10% for sulfur were obtained by several authors in intercomparison experiments (Wätjen et al., 1983; Bombelka et al., 1984; Richter et al., 1984; Maenhaut et al., 1987; Cornille et al., 1990). The second possible analytical artifact would be electron beam damage during analysis of the particles. We have used a very low electron current (1 nA) to avoid this potential problem. Several other studies, using identical analytical procedures, some from the same laboratory, show a high presence of particles containing only sulfur as detectable element with  $Z > 11$  (Mészáros and Vissy, 1974; Saucy et al., 1987; Anderson et al., 1988; Artaxo et al., 1988, 1990a, 1990c; Bruynseels et al., 1988;

Van Borm and Adams, 1988; Xhoffer et al., 1991). This leads to the conclusion that for particles larger than  $0.1 \mu\text{m}$  in the Antarctic peninsula, most of the sulfur in the fine mode is in the form of calcium sulfate. Several particle formation mechanisms must be investigated in order to discuss the high presence of CaSO<sub>4</sub>. When a drop of sea-water is emitted to the atmosphere (Blanchard, 1985), progressive evaporation of water and compounds occurs. Different salts crystallize at various rates: calcium carbonate and sodium sulfate are the first to crystallize (Wellman and Wilson, 1963). This process allows for the occurrence of elemental fractionation on freezing of sea-water droplets (Harvey et al., 1991). Harvie et al. (1980) have analyzed the mineral sequences of evaporation of sea-water droplets containing CaSO<sub>4</sub>, and showed the fractionation sequence for some compounds. Another possibility for the mechanism of formation of these CaSO<sub>4</sub> particles is heterogeneous reaction of atmospheric sulfur gases with marine biogenic CaCO<sub>3</sub> (coccoliths) particles (Andreae et al., 1986; Sievering et al., 1991). Also CaCO<sub>3</sub> could react with H<sub>2</sub>SO<sub>4</sub> as a result of aerosol interactions within clouds.

The group of particles in Fig. 7 with silicon and chlorine represents internally mixed silicate/sea-

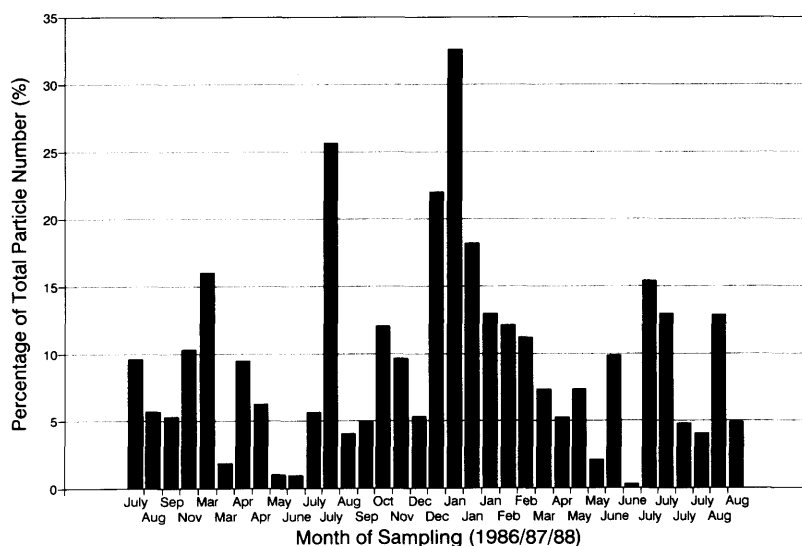


Fig. 8. Seasonal variability of the population of fine mode CaSO<sub>4</sub> particles. (CaSO<sub>4</sub> and CaSO<sub>4</sub> mixed with NaCl and MgCl<sub>2</sub>). From July 1986 to August 1988, 35 individual fine mode aerosol samples were analysed. The percentage of particles belonging to this group to total particle number is shown for each sample.

salt and was also observed over the remote marine atmosphere (Andreae et al., 1986). They probably result from cloud coalescence which brings together mineral particles with sea-salts. This mechanism also leads to interactions between sulfate containing and sea-salt containing droplets and causes enrichment of sulfates in sea-salt particles (Sievering et al., 1991). There is a significant

number of NaCl and  $\text{MgCl}_2$  particles showing small amounts of sulfur. The marine aerosol particles cycle several times through cloud formation and evaporation processes, leading to sulfur excess in the particles and enrichment of several compounds at the individual particle level (Fitzgerald, 1991).

Fig. 8 shows the seasonal variability of the

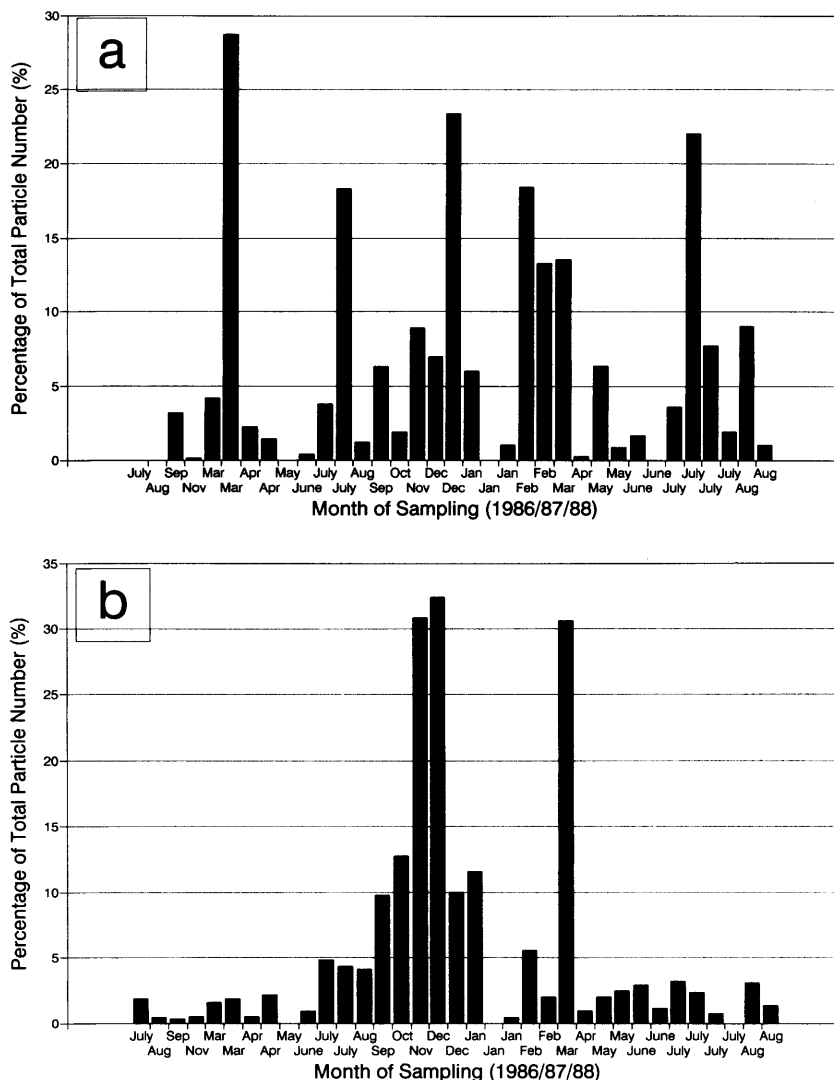


Fig. 9. Seasonal variability of fine mode antarctic aerosol particles. (a)  $\text{MgCl}_2$  particles. (b) Si mixed with NaCl. The morphology of these silicon particles suggest that some of these particles are skeletons of marine organisms. From July 1986 to August 1988, 35 individual fine mode aerosol samples were analysed. The percentage of particles belonging to this group to total particle number is shown for each sample.

population of  $\text{CaSO}_4$  particles for the fine mode. During summertime, the population of  $\text{CaSO}_4$  particles is maximum, suggesting a biogenic origin for the sulfur in these particles. However, the formation mechanisms of these particles are not clear to us. Possibly other mechanisms in addition to the bursting of air bubbles are taking place (Blanchard and Woodcock, 1957, 1980; Lovett, 1978; Stramska et al., 1990). In-cloud processes could be responsible for the production of part of these  $\text{CaSO}_4$  particles (Andreae et al., 1986). The process of sequential evaporation of sea-water droplets can also release these  $\text{CaSO}_4$  particles in the atmosphere (Harvie et al., 1980). Heterogeneous reactions of long-range transported  $\text{CaCO}_3$  with marine biogenic sulfur is also a possibility (Sievering et al., 1991). There is no clear seasonal variability for the average particle diameter for the fine mode  $\text{CaSO}_4$  particle group. The average particle diameter varies between  $0.25\ \mu\text{m}$  and  $0.6\ \mu\text{m}$ .

The other particle types do not show a seasonal variability, as can be seen in Fig. 9a for  $\text{MgCl}_2$  particles and in Fig. 9b for particles containing Si and chlorine. The morphology of these silicon particles suggests that they are skeletons of marine organisms.

## 5. Conclusions

The aerosol in the Antarctic peninsula is dominated by sea-salt particles. Small amounts of soil dust and sulfates also are observed. From the bulk elemental concentrations in the fine mode, these three aerosol components are clearly discriminated. In the coarse mode, sea-salt and soil dust components can be separated on the basis of the temporal variability of the elemental concentrations. Some elements like Cr, Ni, Cu, Zn, and Pb appear too high in concentration, showing high enrichment values, possibly indicating local or regional air pollution contamination. The non-sea-salt sulfur concentration shows a seasonal variability, with higher concentrations during summertime. The elemental source profile obtained

by a absolute principal factor analysis for the sea-salt component is remarkably similar to the average bulk sea-water composition for both the fine and coarse mode aerosol components. This indicates low enrichment for the major elements. Analyzing a large number of individual aerosol particles, it was observed that sulfur for particles in the size range  $0.1\ \mu\text{m} < d_p < 2.0\ \mu\text{m}$  appears preferentially as  $\text{CaSO}_4$  instead of the expected  $(\text{NH}_4)_2\text{SO}_4$  or  $\text{NH}_4\text{HSO}_4$ . The seasonal variability of these  $\text{CaSO}_4$  particles shows a higher population during summertime. There are several possible mechanisms that could be responsible for these  $\text{CaSO}_4$  particles. Other types of sea-salt particles observed in large numbers were NaCl and  $\text{MgCl}_2$ . Also pure silicon particles and Si mixed with NaCl were observed, in addition to soil dust particles. A large number of NaCl and  $\text{MgCl}_2$  particles show small (around 1%) amounts of sulfur, possibly indicating reactions of these particles with gaseous sulfur compounds.

The combination of bulk analytical techniques with microanalytical techniques, giving concentrations at the individual particle level, was very powerful. These two completely independent analyses complement each other ideally, giving a more clear view of aerosol particle properties than if used alone.

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